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(21) International Application Number: PCT/FI98/00391 (22) International Filing Date: 7 May 1998 (07.05.98) (30) Priority Data: 971973 7 May 1997 (07.05.97) FI (71) Applicant (for all designated States except US): NESTE OYJ [FI/FI]; Keilaniemi, FIN-02150 Espoo (FI). (72) Inventors; and (75) Inventors/Applicants (for US only): KOISTINEN, Jari [FI/FI]; Lamminmutka 2 C 14, FIN-40520 Jyväskylä (FI). RIS-SANEN, Kari [FI/FI]; Hankamäenti 13, FIN-41520 Hankasalmi (FI). KOSKIMIES, Salme [FI/FI]; Hämeenapajantie 7, FIN-00850 Helsinki (FI). (74) Agents: LAINE, Seppo et al.; Seppo Laine OY, Itämerenkatu 3B, FIN-00180 Helsinki (FI).	(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>In English translation (filed in Finnish).</i>	
(54) Title: PROCESS FOR PREPARING AND PURIFYING COMPLEX ESTERS		
(57) Abstract <p>The invention concerns a process for manufacturing polyol complex esters. According to the method, a polyol, such as BEPD or NPG, is reacted with mono- and polyvalent acids in the presence of a catalyst to produce a reaction blend containing complex esters. According to the invention the acid components of the reaction blend are neutralized with a tertiary amine, and the complex esters are recovered from the thus treated reaction blend. The basic amines that are used form salt-like compounds with the carboxylic acids. The compounds enter the aqueous phase, from which they are easily separated, whereby the complex esters are recovered with high yield.</p>		

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PROCESS FOR PREPARING AND PURIFYING COMPLEX ESTERS

5 The present invention concerns a process according to the preamble of claim 1 for the preparation and purification of complex polyol esters.

10 According to the process, a mixture of complex esters is made by reacting a polyol with mono- and polybasic acids in the presence of a catalyst, the reaction mixture is treated with a base to neutralize the acid components, and the complex esters are retrieved from the thus treated reaction mixture.

15 Complex polyol esters can be used as lubricant base stocks, which can serve as complete lubricants, or as compounded lubricants with, e.g., hydrocarbon lubricants, to improve the biodegradability of said products, as biodegradable hydraulic oils, compressor oils, metal working fluids, and with chlorine-free, fluorine-containing refrigerants as the fluid lubricant component in refrigerator compressors.

20 The general manufacturing of polyol esters is known. A considerable problem is, however, the purification of the final products, especially the removal of acid impurities (the carboxylic acids that did not react), because many methods used for neutralizing and extraction give rise to emulsions that are difficult to separate. Strong inorganic bases, i.e. sodium hydroxide, or basic salts, i.e. sodium carbonate or sodium bicarbonate, are usually used in the neutralizing process. Also hot-neutralizing methods are known. The strong bases decompose the desired ester product and cause the formation of emulsions. Various
25 difficult steps of refining and distillation are needed after neutralization, as mentioned for example in SE Patent Application No. 7400019-1.

The technical solution described in the DE Published Patent Application No. 1 444 851 can be mentioned as an example of the prior art: a raw ester product originating in complex
30 esterification of trimethylpropane is first diluted with petrol ether, after which it is washed with a 5 % aqueous solution of sodium hydroxide to neutralize the remaining acid. Washing is continued with a 12 % sodium chloride solution until the mixture is neutral. Active carbon is subsequently added, and then the mixture is heated at low pressure to 160 - 180 °C, in order to remove the water, petrol ether and volatile impurities.

35

The yield of complex esters is quite low after such elaborate cleansing operations.

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It is an aim of the present invention to remove the disadvantages of the prior art, and to provide a completely new method for the production and purification of complex esters.

The invention is based on the concept that complex polyol esters can be produced with good yield, by using organic bases, in particular tertiary amines, to neutralize the acid components, and by extracting the impurities into an aqueous solution. The tertiary amine used comprises an amine according to the formula $R^1R^2R^3N$, wherein R^1 , R^2 , and R^3 independently represent alkyl groups, having 1 - 5 carbon atoms, and/or aryl groups, and R^1 and R^2 can together form a substituted or unsubstituted ring, having 5 - 10 carbon atoms.

More specifically, the technical solution according to the invention is mainly characterized by what is stated in the characterizing part of claim 1.

The separation of the viscous complex esters is significantly easier with the present method than with conventional neutralization methods employing $NaHCO_3$, Na_2CO_3 or $NaOH$, or using hot neutralization. The amines are basic, but they do not directly react with the carboxylic acids, instead they form salt-like complexes. These enter the aqueous phase, from which they are easily separated. The amines do not as easily form emulsions as strong inorganic bases do, and no solvents are necessarily needed for the cleansing.

In the following the invention will be discussed with the aid of a detailed description and some working examples. The enclosed figures show the LC product analysis according to Example 2 and the HPGPC product analysis of the product of Example 6.

This invention concerns in particular the manufacture of polyol-based complex esters in the case when the polyol is a sterically hindered, alpha-substituted diol, such as 2-butyl-2-ethyl-1,3-propanediol (BEPD), neopentyl glycol (NPG), hydroxypivalyl hydroxypivalate (HPPH), or a triol, such as trimethylolpropane (TMP), trimethylolethane (TME) or pentaerythritol (PE). An important advantage of these sterically hindered polyols is their stability, which is important both for lubricant and refrigerant applications.

Mono- and polybasic carboxylic acids are used for the manufacturing of esters. Preferred carboxylic acids according to the invention are mixtures of C_5 - C_{18} monocarboxylic and dicarboxylic acids. The monocarboxylic acids may be either linear or branched, hydroxy acids (that is, they contain both a carboxylic and hydroxylic group) or they can contain double bond(s) (unsaturated).

Suitable monocarboxylic acids are for instance octanoic acid and 2-ethylhexanoic acid. A suitable hydroxy acid is hydroxypivalic acid (HPAA) and oleic acid can be mentioned as an unsaturated acid.

5 Examples of dicarboxylic acids are oxalic acid, malonic acid, dimethylmalonic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, pimelic acid, suberic acid and azelaic acid. Preferred dicarboxylic acids are adipic acid, sebacic acid and azelaic acid. Furthermore the carboxylic acid can be a mixture of one or several of the acids mentioned above together with dimethylmalonic acid or a cyclic anhydride, such as alkenyl succinic
10 acid, or trimellitic anhydride.

In the method according to the invention all the reactants (polyol, catalyst, mono- and dicarboxylic acid) are weighed into the reactor and heated for 3 - 10 h, preferably 5 - 8h at 180 - 240 °C, preferably at 200 - 220 °C, until the acid number has decreased below 10 mg
15 KOH/g. The molar ratio of the reactant di- and monoacids is in the range 5:95 - 40:60 mol %, typically 10:90 - 30:70 mol %. The esterification is preferably done by using catalyst acids, such as p-toluenesulphonic acid, sulphuric acid, hydrochloric acid, or metal oxides, such as titanates or tin oxides. The amount of catalyst used is typically 0.05 - 0.5 % of the reacting components.

20 Since the esterization reaction is a condensation reaction, in which water is released, a low flow of protective gas (e.g. nitrogen) is maintained in order to make the removal of water more effective. Most preferably the protective gas is bubbled through the reaction mixture.

25 As a medium for the esterization an organic solvent can be used, which is inert with respect to the reactants, for example hydrocarbon with low boiling temperature, such as heptane, or a hydrocarbon mixture with high boiling temperature, such as LIAV 270. The solvent is added at the same time as the other reagents to the reactor. The amount of solvent is ca 10-50 weight-%, preferably ca 20-40 weight-% of the reactants.

30 After the reaction has come to an end the catalyst is filtered away. The filtering is preferably done when the reaction mixture is still hot, because filtering is then easier.

To neutralize the remaining acid, an amine is added to the cooled reaction mixture. The
35 amine has the formula $R^1R^2R^3N$, wherein R^1 , R^2 and R^3 represent independent alkyl groups, with 1 - 5 carbon atoms, or aryl groups; and R^1 and R^2 may together form a substituted or

unsubstituted ring with 5 - 10 carbon atoms. Preferably R^1 and R^2 represent lower alkyl groups, such as methyl and ethyl, whereby especially preferred amines are trimethylamine and triethylamine. Other tertiary amines are tri-n-propylamine, tri-n-butylamine, tri-isobutylamine, tri-n-amylamine, triisoamylamine and methyl diethylamine. Examples or
5 aromatic amines to be mentioned are dimethylaniline, triphenylamine, diethylaniline and ethylbenzylaniline.

The amount of amine fed into the reaction mixture is ca 0.1 - 30 weight-%, preferably ca 0.5 - 15 weight-%, in particular ca 1-10 weight-% (for example ca 2-5 weight-%).
10 Thereafter the mixture is blended at 20 - 100 °C, preferably at 60 - 90 °C, for a suitable length of time. The blending time varies with the amount of acid components, typically from a couple of minutes to several hours. Usually the mixing takes ca 1 - 10 h.

According to a preferred embodiment, an organic solvent is used for the washing. The
15 solvent promotes the separation and allows for a further increase of the yield. For the washing a similar solvent can be used as in the esterification reaction, that is for example an organic solvent with low boiling temperature, such as heptane, or a hydrocarbon mixture with high boiling temperature. If an organic solvent with low boiling temperature is used in the washing phase, the solvent is added to the reaction mixture before the base.
20 The amount of solvent is 10 - 50 weight-%, most preferably 20 - 40 weight-% of the reactants.

After the alkaline washing, the impurities are extracted with water. Thus, water is added to the neutralized mixture in such a way that the amount of water is at least about the same as
25 that of the base, that is ca 0.1 - 30 weight-%, preferably ca 0.5 -15 weight-% of the reaction mixture. The amine-carboxylic acid complex or salt formed in the neutralizing reaction is separated and the emulsion that may have been formed is salted out with NaCl-solution. After this the reaction mixture is washed with dilute mineral acid (for example ca 0.5 - 2 M hydrochloric or phosphoric acid) and thereafter once or twice with warm water. The final
30 product is dried with a drying agent, for example, on sodium sulphate, and filtered. If a solvent has been used, it is removed with vacuum distillation (2 - 3 h, 1 mbar, 200 - 230 °C) after washing with water, and filtered.

The following examples illustrate the method according to the invention. In Examples 1-31
35 2-butyl-2-ethyl-1,3-propanediol has been used as polyol, and in Examples 32-38 neopentyl glycol, trimethylolpropane, hydroxypivalyl hydroxypivalate and pentaerythritol. In

Example 4 a solvent has been added in the cleansing phase.

Examples 1-3 and 5-31

5 Complex esters of BEPD (2-butyl-2-ethyl-1,3-propanediol) were manufactured by loading the reactor vessel with BEPD and saturated linear or branched monocarboxylic acid (C_5 - C_{16}) or unsaturated carboxylic acid (C_{14} - C_{22}) and diacid (adipic, sebacic), whereby 1 mol % of monoacid was used in excess of alcohol. The amount of the tin oxide catalyst (Tekokat 188) was 0.15 weight-% of the amount of reagent. The reaction blend was heated
10 to 200 -220 °C in nitrogen atmosphere and was kept at this temperature for ca 7 hours, or until the acidity had decreased below 10 mg KOH/g. After the blend had been cooled, an organic base (triethylamine) was added at an amount of 5 - 15 weight-% of the amount of reagents. The blend was heated to 80 °C and mixed for ca 3 hours. The blend was washed once or twice with a small amount of water (base:water 1:1). Excess base was washed
15 away with 0.5 - 1.0 M mineral acid (HCl, H_3PO_4). Eventually the blend was washed once or twice with water and dried with Na_2SO_4 .

The products obtained with different acids and varying molar ratios are presented together with their properties in Tables 1-10 and a typical LC-product analysis of the product
20 according to Example 2 is presented in Figure 1.

Example 4

The reactants (BEPD, catalyst, adipic acid and octanoic acid and solvent) were measured
25 into a rector and heated for 7 h 200 -220 °C. A low flow of nitrogen was maintained in order to make the removal of water more efficient. A solvent mixture (LIAV 270) with high boiling temperature was used for solvent, its amount was 30 % of the reactants. After the reaction had come to its end, the catalyst was filtered away while the reaction blend was still hot. After the reaction mixture had cooled, 3 weight-% triethylamine was added,
30 and the mixture was blended for ca 3 hours at 70 - 80 °C.

After purification of the base, water was added at the same amount as base. The salt that had formed was separated and the emulsion that might have formed was salted out with NaCl-solution. Thereafter the reaction blend was washed with dilute HCl and twice with
35 warm water. The end-product was dried with Na_2SO_4 and filtered.

The properties of the product are presented in Table 1 (Example 4).

Examples 32 - 38

- 5 The reaction was performed as in the Examples 1-3 and 5-31, with the distinction that the polyol used was NPG, TMP, HPHP or PE.

10 **Tables 1 - 4. Properties of BEPD complex esters.**

Table 1. BEPD + adipic acid + octanoic acid

Example No./ acid mol-%	V ₁₀₀ mm ² /s	V ₄₀ mm ² /s	VI	PP °C	Acid No. mg KOH/g	Yield %
1. 10/90	3.84	17.4	112	-60	0.05	71
15 2. 20/80	5.33	28.2	125	-54	0.3	58
3. 30/70	7.54	47.3	124	-45	1.9	36
4.* 30/70	7.51	44.9	133	-42	0.79	69

*solvent 30 weight % (LIAV 270)

20 **Table 2. BEPD + adipic acid + nonanoic acid**

Example No./ acid mol-%	V ₁₀₀ mm ² /s	V ₄₀ mm ² /s	VI	PP °C	Acid No. mg KOH/g	Yield %
5. 10/90	4.30	20.2	121	-57	1.0	72
25 6. 20/80	5.78	31.8	125	-51	1.0	65
7. 30/70	8.43	53.5	131	-51	< 0.1	41

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Table 3. BEPD + adipic acid + decanoic acid

Example No./ acid mol-%	V ₁₀₀ mm ² /s	V ₄₀ mm ² /s	VI	PP °C	Acid No. mg KOH/g	Yield %
8. 10/90	4.83	23.1	134	-54	1.1	79
9. 20/80	6.59	36.5	137	-54	0.93	60
10. 30/70	9.28	60.5	133	-48	3.3	54

Table 4. BEPD + adipic acid + dodecanoic acid

Example No./ acid mol-%	V ₁₀₀ mm ² /s	V ₄₀ mm ² /s	VI	PP °C	Acid No. mg KOH/g	Yield %
11. 10/90	5.90	30	145	-	2.2	43
12. 20/80	6.3	34.9	132	-39	0.14	56
13. 30/70	10.4	68.4	139	-36	1.0	53

Table 5. BEPD + adipic acid + oleic acid

Example No./ acid mol-%	V ₁₀₀ mm ² /s	V ₄₀ mm ² /s	VI	PP °C	Acid No. mg KOH/g	Yield %
14. 10/90	8.04	41.1	173	-39	1.4	74
15. 20/80	9.88	54.0	172	-42	0.9	59
16. 30/70	11.9	72.1	161	-42	0.35	66

Table 6. BEPD + sebacic acid + octanoic acid

Example No./ acid mol-%	V ₁₀₀ mm ² /s	V ₄₀ mm ² /s	VI	PP °C	Acid No. mg KOH/g	Yield %
17. 10/90	4.32	20.0	124	-60	0.6	76
18. 20/80	6.66	36.5	140	-54	1.56	63
19. 30/70	10.6	68.7	142	-54	2.1	55

Table 7. BEPD + sebacic acid + nonanoic acid

Example No./ acid mol-%	V ₁₀₀ mm ² /s	V ₄₀ mm ² /s	VI	PP °C	Acid No. mg KOH/g	Yield %
20. 10/90	4.76	22.8	132	-60	1.3	78
21. 20/80	7.16	40.0	143	-54	1.9	68
22. 30/70	9.41	64.4	125	-51	1.6	62

Table 8. BEPD + sebacic acid + decanoic acid

Example No./ acid mol-%	V ₁₀₀ mm ² /s	V ₄₀ mm ² /s	VI	PP °C	Acid No. mg KOH/g	Yield %
23. 10/90	5.31	25.9	143	-54	1.6	69
24. 20/80	7.78	44.2	147	-51	2.6	56
25. 30/70	7.22	41.6	137	-45	1.3	48

Table 9. BEPD + sebacic acid + dodecanoic acid

Example No./ acid mol-%	V ₁₀₀ mm ² /s	V ₄₀ mm ² /s	VI	PP °C	Acid No. mg KOH/g	Yield %
26. 10/90	6.98	37.1	152	-27	2.3	57
27. 20/80	9.05	52.8	153	< -30	1.0	61
28. 30/70	13.1	87.5	149	-36	2.7	51

Table 10. BEPD + sebacic acid + oleic acid

Example No./ acid mol-%	V ₁₀₀ mm ² /s	V ₄₀ mm ² /s	VI	PP °C	Acid No. mg KOH/g	Yield %
29. 10/90	8.61	43.7	180	-39	2.4	71
30. 20/80	11.2	62.5	174	-39	2.2	55
31. 30/70	15.2	94.9	169	<-30	2.8	29

Tables 11 - 13. Properties of other polyol complex esters.

Table 11. NPG + adipic acid + nonanoic acid

Example No./ acid mol-%	V ₁₀₀ mm ² /s	V ₄₀ mm ² /s	VI	PP °C	Acid No. mg KOH/g	Yield %
32. 20/80	4.47	19.0	155	< -30	1.6	64

Table 12. NPG + sebacic acid + nonanoic acid

Example No./ acid mol-%	V ₁₀₀ mm ² /s	V ₄₀ mm ² /s	VI	PP °C	Acid No. mg KOH/g	Yield %
33. 20/80	5.75	25.5	179	< -39	0.8	59

Table 13. HPHP + adipic acid + octanoic acid

Example No./ acid mol-%	V ₁₀₀ mm ² /s	V ₄₀ mm ² /s	VI	PP °C	Acid No. mg KOH/g	Yield %
34. 20/80	7.06	39.8	140	-51	1.0	66

Table 14. HPHP + sebacic acid + nonanoic acid

Example No./ acid mol-%	V ₁₀₀ mm ² /s	V ₄₀ mm ² /s	VI	PP °C	Acid No. mg KOH/g	Yield %
35. 20/80	8.79	50.5	154	-51	0.15	62

Table 15. TMP + adipic acid + nonanoic acid

Example No./ acid mol-%	V ₁₀₀ mm ² /s	V ₄₀ mm ² /s	VI	PP °C	Acid No. mg KOH/g	Yield %
36. 20/80	13.6	92.2	149	-45	0.57	68

Table 16. TMP + adipic acid + nonanoic acid

Example No./ acid mol-%	V ₁₀₀ mm ² /s	V ₄₀ mm ² /s	VI	PP °C	Acid No. mg KOH/g	Yield %
37. 20/80	19.3	135.9	162	-45	0.8	45

5

Table 17. PE + adipic + nonanoic acid

Example No./ acid mol-%	V ₁₀₀ mm ² /s	V ₄₀ mm ² /s	VI	PP °C	Acid No. mg KOH/g	Yield %
38. 10/90	12.9	86.9	147	<-30	0.36	59

10

Claims:

1. A process for the production of complex polyol ester with high yield, according to which method

- a polyol is reacted with mono- and polybasic acids in the presence of a catalyst to produce a reaction blend containing complex esters,
- the reaction blend is treated with a base to neutralize the acid components, and
- the complex esters are recovered from the reaction blend treated in this manner,

characterized by that

- the acid components of the reaction blend are neutralized with a tertiary amine having the formula $R^1R^2R^3N$, wherein R^1 , R^2 and R^3 represent independent alkyl groups with 1 - 5 carbon atoms, and aryl groups, and R^1 and R^2 can together form a substituted or unsubstituted ring with 5 - 10 carbon atoms.

2. The process according to claim 1, wherein 2 to 5 weight - % tertiary amine is added to the reaction blend.

3. The process according to claim 1 or 2, wherein the reaction blend is treated with tertiary amine at a temperature of in the range of 20 to 100 °C.

4. The process according to any of the preceding claims, wherein the reaction blend is treated with tertiary amine in an organic solvent.

5. The process according to claim 4, wherein the amount of organic solvent is ca 10 to 50 weight- % of the reaction blend.

6. The process according to any of the preceding claims, wherein the tertiary amine used is an aliphatic amine, such as trimethylamine, triethylamine, tri-n-propylamine, tri-n-butylamine, triisobutylamine, tri-n-amylamine, triisoamylamine or methyl-diethylamine, or an aromatic amine, such as dimethylaniline, triphenylamine, diethylaniline or ethylbenzyl aniline.

7. The process according to one of the claims above, wherein water is added to the reaction blend after the amine treatment and the salts thus formed are separated.

8. The process according to claim 7, wherein the amount of water is at least

approximately the same as that of amine.

5 9. The process according to claim 7 or 8, wherein the reaction blend is washed and the complex esters are recovered by separating the solid impurities and the solvent, if present, from the reaction blend.

10 10. The process according to one of the claims above, wherein the polyol is a sterically hindered, alpha-substituted diol, such as 2-butyl-2-ethyl-1,3-propanediol, neopentyl glycol, hydroxypivalyl hydroxypivalate, or a triol, such as trimethylolpropane, trimethylol ethane or pentaerythritol.

11. The process according to one of the claims above, wherein the carboxylic acid is a mixture of C₅-C₁₈ monocarboxylic acids and dicarboxylic acids.

15 12. The process according to claim 11, wherein the monocarboxylic acid is linear or branched, a hydroxy acid or it contains a double bond.

20 13. The process according to claim 12, wherein the monocarboxylic acid is octanoic acid, 2-ethylhexanoic acid, hydroxypivalic acid or oleic acid.

25 14. The process according to any of claims 11 - 13, wherein the dicarboxylic acid is oxalic acid, malic acid, dimethylmalic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, pimelic acid, suberic acid or azelaic acid, or a cyclic anhydride, such as succinic anhydride or an alkyl derivative thereof, or trimellitine anhydride.

30 15. The process according to any of claims 11 - 14, wherein the molar ratio of di- and monoacids is in the range from 5:95 to 40:60 mol-%, typically 10:90 - 30:70 mol %.

35 16. The process according to any of the claims above, wherein the amount of catalyst used is 0.05-0.5 % of the amount of the reactants.

17. The process according to claim 16, wherein an acid catalyst is used, such as p-toluene-sulphonic acid, sulphuric acid or hydrochloric acid, or a metal oxide, such as tin oxide or titanate.

18. The process according to any of the preceding claims, wherein the reaction time of the

esterification is 3 - 10 h, preferably 5 - 8 h, at 180-240 °C, in order to reduce the acid number below 10 mg KOH/g.

- 5 19. The process according to any of the preceding claims, wherein the solvent used in the reaction phase is a non-polar hydrocarbon, such as heptane, or a hydrocarbon mixture with high boiling temperature, such as LiAV 270.

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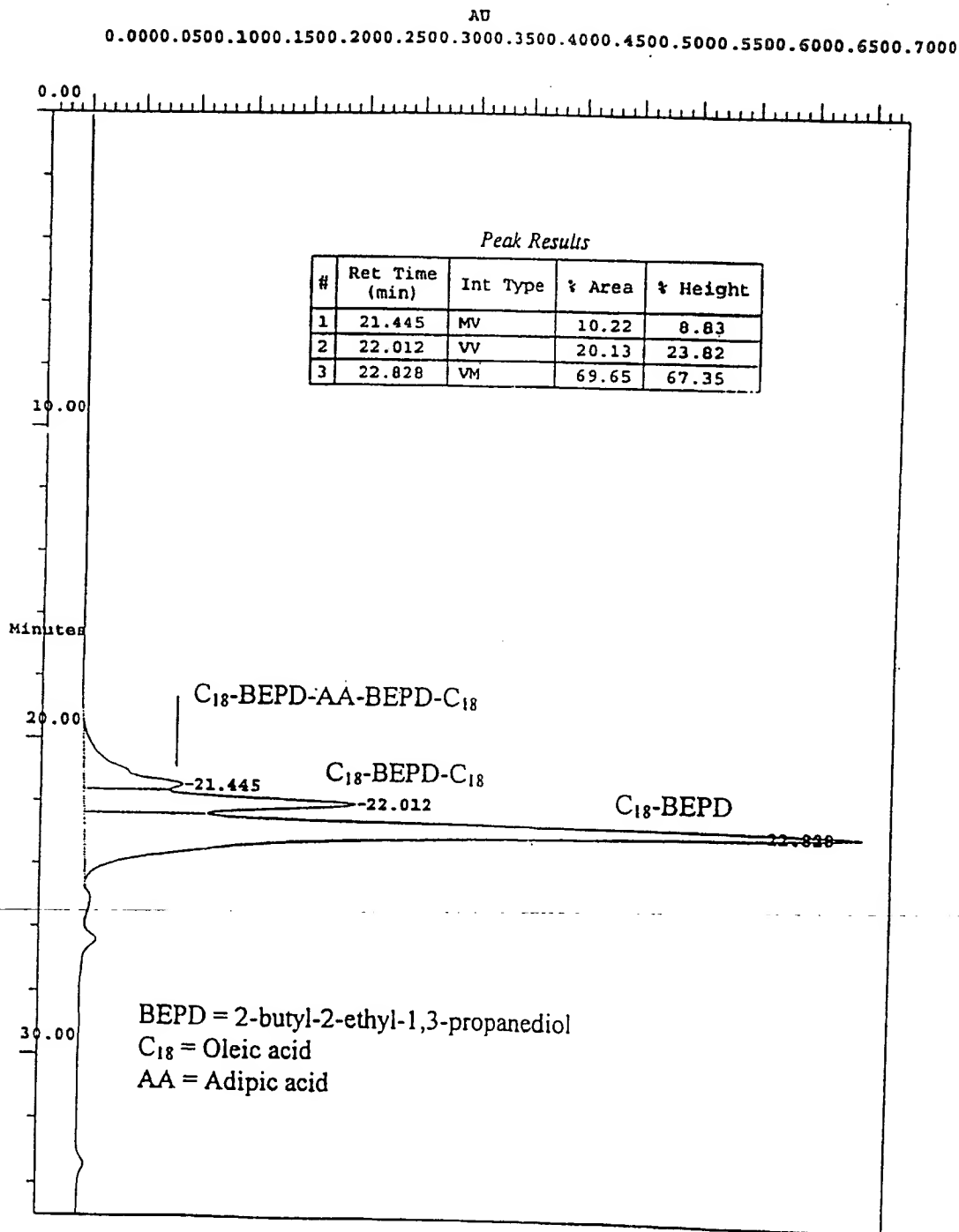
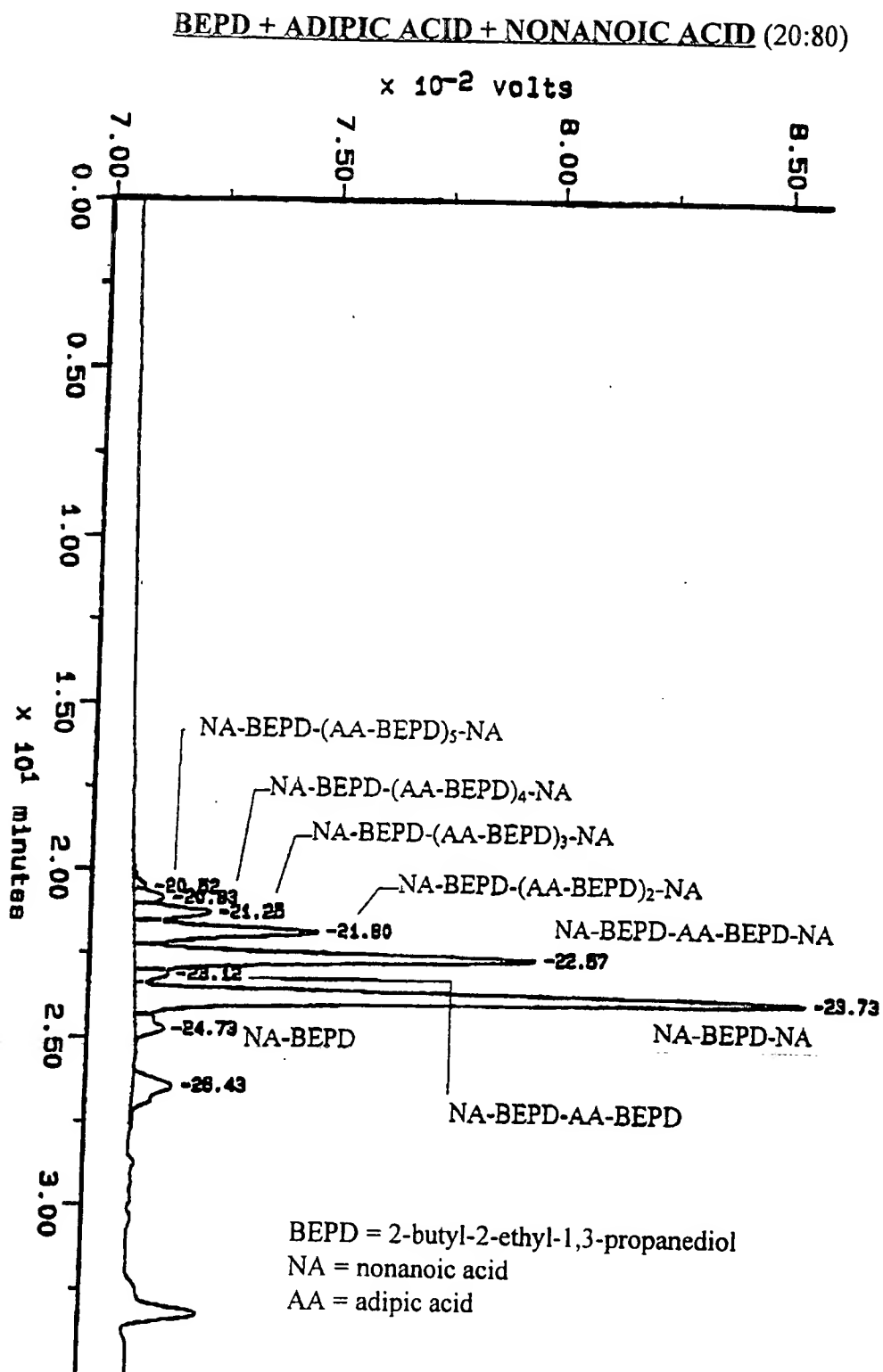


Fig. 1

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Column: Plgel 500, 100, 100 Å, 5 µm, 300 x 7.5 mm. Eluent: THF. Detector: UV 230 nm

Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 98/00391

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C07C 67/48, C07C 67/08, C07C 67/58, C07C 67/60
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4405471 A (MANS O. MANSON ET AL), 20 Sept 1983 (20.09.83)	1-19
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A	WO 9116296 A1 (HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN), 31 October 1991 (31.10.91)	1-19
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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

30/06/98

International application No.

PCT/FI 98/00391

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4405471 A	20/09/83	AT 372399 B	26/09/83
		AT 390055 B	12/03/90
		BE 887689 A	15/06/81
		CH 648343 A,B	15/03/85
		DE 3107052 A,C	24/12/81
		DK 89181 A	30/08/81
		DK 161714 B,C	05/08/91
		FI 69865 B,C	31/12/85
		FI 810635 A	30/08/81
		GB 2072661 A,B	07/10/81
		NL 189308 B,C	01/10/92
		NL 8100954 A	01/10/81
		SE 452772 B,C	14/12/87
		SE 8101108 A	30/08/81
WO 9116296 A1	31/10/91	DE 4012693 A	24/10/91

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